

(72) PY, CHRISTOPHE, CA

(71) NATIONAL RESEARCH COUNCIL OF CANADA, CA

(51) Int.Cl.⁷ H01L 21/302, H01L 21/312, G02B 6/136

(54) **SEPARATEUR INORGANIQUE DE COUCHES ORGANIQUES A
MICRO-MOTIFS**

(54) **AN INORGANIC SEPARATOR STACK TO MICRO-PATTERN
ORGANIC LAYERS**



**material
discontinuous
et edge of
separator**

(57) A patterned layer of organic material is formed on a substrate by depositing a composite stack of at least two inorganic layers on the substrate. The inorganic layers have different etch rates, with the upper layer having a lower etch rate than the underlying layer. The composite stack is masked to leave exposed portions defining a pattern. The exposed portions are then etched away to form a separator with an overhang resulting from the different etch rates of the layers. An organic layer is deposited on the resulting structure using a directional deposition technique to form a patterned organic layer.

ABSTRACT OF THE DISCLSOSURE

A patterned layer of organic material is formed on a substrate by depositing a composite stack of at least two inorganic layers on the substrate. The inorganic layers have different etch rates, with the upper layer having a lower etch rate than the underlying layer. The composite stack is masked to leave exposed portions defining a pattern. The exposed portions are then etched away to form a separator with an overhang resulting from the different etch rates of the layers. An organic layer is deposited on the resulting structure using a directional deposition technique to form a patterned organic layer.

AN INORGANIC SEPARATOR STACK TO MICRO-PATTERN ORGANIC LAYERS

Field of the invention

The present invention relates to a method of fabricating electronic components and devices using organic materials for use, for example, as flat-panel displays, as
5 semiconductors or conductors for electronic components such as transistors, or in passive or active optoelectronic components such as waveguides, modulators or solid-state lasers.

Background of the invention

Organic materials show promise for electronic and optoelectronics applications, either by bringing additional functionality or by replacing existing components and devices at
10 lower cost. For example, organic materials can advantageously be used as electroluminescent materials because they can produce all colors of the spectrum, can be deposited on flexible substrates, work at much lower voltages and cost much less than their inorganic counterparts.

However, organic materials are generally incompatible with the standard microfabrication
15 techniques used for inorganic materials. Microfabrication is based on the repetitive use of lithography, where a photosensitive resin 10 is used to transfer a pattern from a mask 12 to the material(s) of interest (see Fig. 1a), in this case layer 14 on substrate 16. The resin 10 is selectively exposed to ultra-violet light through the mask 12 to induce a photochemical modification. An alkaline solution thereafter referred to as a developer
20 dissolves the exposed resin (Fig 1b), leaving the remaining resin 10 with the same pattern as the mask 12. The resin 10 is then used as a mask to selectively etch the underlying layer(s) 14 (Fig 1c). When the pattern has been transferred, the resin is stripped selectively to the underlying layer(s) 14 in a solution thereafter referred to as a stripper (Fig 1d). This basic technique can generally not be used for organic materials because
25 their similar nature to the photosensitive resin means an absence of selectivity. The organic materials to be patterned would be contaminated by the photosensitive resin solvent, or dissolved by the developer or by the stripper. Furthermore, the photosensitive resin has to undergo thermal treatments before being exposed and generally after being developed, and the temperatures involved are higher than the glass transition temperatures
30 of some of the organic materials of interest.

An alternative patterning technique is the use of a shadow mask 20 for those organic materials that can be deposited in a directional manner, generally by evaporation in a high-vacuum chamber (Figure 2a). However, either the shadow mask 20 is in direct contact with the substrate 16 on which the organic material is going to be deposited, and damage might occur, or it is not in contact (as illustrated), in which case the method can only provide low resolution patterns. Moreover, this technique is not suitable for polymers that are difficult to deposit in a directional manner. Silver screen printing, where materials 14 are directly coated (for example, painted) on a mask 22 and substrate directly in contact (Fig 2b) before removing the mask, provides very low resolution patterns and is limited to certain materials.

Some organic materials have electroluminescent properties (they will be thereafter referred to as OELs) and can be used in organic electroluminescent displays (Figure 3). In this technology, light is obtained from organic electroluminescent layer(s) 48 sandwiched between conductive layers, an anode and a cathode, at least one of each being transparent. When sufficient positive voltage is applied between the anode 30 and the cathode 32, the OELs produce light observed through the transparent electrode(s). The display can be addressed by a XY passive matrix (as shown in Figure 3). The display shown in Figure 3 is seen through the transparent substrate. The anode, also transparent, is formed in columns, while the cathode, not transparent, is formed in rows perpendicular to the columns so the entire display can be addressed in individual pixels at the intersection of each row and column.

US patent 5,701,055 teaches a structure that can be specifically applied to organic electroluminescent displays. The anode formed on a substrate is first etched in columns by a conventional microfabrication technique. Then ramparts with an overhanging edge are patterned on the substrate in rows across the anode columns. OELs are formed on this structure; then the cathode is deposited orthogonally to the substrate, such that this conductive layer is discontinuous at the edges of the ramparts. A matrix is obtained without the need to pattern the cathode on top of the OELs. The patent further describes means to prevent short-circuits occurring between the anode and the cathode when the cathode material flows above the edge of the OELs and directly touches the anode.

However, the method described in patent US 5,701,055 involves patterning two separate structures in a rather complicated process. A first insulating layer 14 is formed on substrate 16 (Fig 4a) and patterned in rows by lithography. The resulting structures are thereafter referred to as inter-insulators (Fig 4b). Then two other insulating layers 40, 42
5 are formed (Fig 4c) and patterned by lithography using a different etching method for each insulating layers (Fig 4d and e). These steps form the ramparts 44. The inter-insulators 14 lie under the edge of the ramparts 44 so that the cathode 46 flowing above the edge of the OELs 48 will not touch the anode (Fig 4f). The method requires two lithographic steps with two different masks and a precise alignment between the two
10 resulting patterns, as well as at least two separate deposition steps and three etching steps.

As an alternative to forming an inter-insulator, a method of preventing cathode to anode short-circuits is described where the substrate is tilted and rotated during deposition of the OELs so as to cover the anode under the overhang of the ramparts. The cathode is then deposited in a directional manner and orthogonally to the substrate so as to be
15 discontinuous at the edges of the rampart. This requires two different vacuum systems so either the sample will be exposed to air between the two systems, resulting in degradation of the OELs, or a costly and complex transfer mechanism in a neutral atmosphere will be needed.

Additionally, the patent describes the use of organic materials themselves for the rampart,
20 such as the use of a photosensitive resin with a reversed tapered edge that saves the need of two different etching steps. However, the use of organic materials as a rampart material results in a display that is not defect-tolerant, yielding low success rates in fabrication. From a microfabrication point of view, one of the great difficulties of making flat-panel displays is that they are large area devices but tolerate very few or no defects.
25 To circumvent the need of high-cost ultra-clean equipment and. avoid low yields, devices must therefore be defect-tolerant. Very often it simply means burning out the defects by injecting sufficient current, so that they will be disconnected from the addressing matrix. That is not possible with a rampart based on organic materials since burning the defect will carbonize the rampart, rendering it conductive and shorting the matrix.

30 US patent 5,294,869 teaches a similar structure where ramparts with an overhang are replaced with high straight walls 50 (see Figure 5) and evaporated material 52 is

directionally deposited at an angle. OELs and the cathode are discontinuous in the shadow of those straight walls when deposited by a directional method (such as evaporation) with a tilt. However, forming high aspect ratio walls is difficult and therefore the method has a limited resolution. Even if such high aspect ratio walls can be
5 formed, their strength will be low and the probability of defects is high, leading to low fabrication yields. The technique also doesn't solve the problem of short-circuits occurring between the anode and the cathode when the latter flows on top of the organic materials edge. Furthermore, the method is only applicable if the walls are elongated in one direction (across which the slanted evaporation takes place). Finally, the method
10 taught in this patent, like in patent US 5,701,055, is limited to materials that can be deposited by a directional method.

SUMMARY OF THE INVENTION

According to the present invention there is provided a method of forming one or more patterned layers of organic material on a substrate, comprising the steps of forming a
15 composite stack of at least two inorganic layers on said substrate, said inorganic layers having different etch rates, with an upper layer having a lower etch rate than an underlying layer; masking said composite stack to leave exposed portions thereof defining a pattern; etching away said exposed portions of said composite layer to form separators with an overhang resulting from the different etch rates of said layers; and depositing an
20 organic layer on the resulting structure to form a patterned organic layer between said separators.

The overhang acts in a similar manner to the ramparts described in the above US patent, but obviates the need to undergo multiple etchings. The use of layers with different etch rates allows the overhang to be formed in a single etch, either by dry or wet etching.
25 Preferably three layers are provided in the composite stack, which may consist of different density materials, although two layers may also be employed in another exemplary embodiment. Also, layers could be of the same density with a different chemical composition provided they etch at different rates in the same etch process.

If the organic material is a monomer or oligomer, it can be evaporated onto the resulting structure. Alternatively, if it is a polymer, it can be spun onto the resulting structure using a spin coater.

A further layer, for example, a metal layer can be deposited on the organic layers.

- 5 The present invention thus provides a method forming separators that is simple, attains very high-resolution patterns and provides a defect tolerant structure. Separators provide a discontinuity of functional layers formed on top of them without the need of further lithography. In the application to organic light emitting displays, the separators also prevent short-circuits between the anode and the cathode without the need for a
- 10 complicated deposition setup and without the need for additional patterning as described in the prior art.

The organic materials can be formed by a directional deposition method, but other methods and can be used; for example, polymers can be formed by spinning. The separators can indeed be advantageously used in any application requiring the patterning

15 of any material that is incompatible with standard microfabrication techniques.

Brief Description of the Drawings

The invention will now be described in more detail, by way of example only, with reference to the accompanying drawings, in which:-

Figure 1a shows a resin applied to a substrate on which a layer is to be etched. Ultra-

20 violet light is shone through a mask and chemically affects the resin where exposed.

Figure 1b shows the resin developed, dissolving where it was exposed.

Figure 1c shows the under layer(s) etched where the resin doesn't mask them.

Figure 1d shows the resin stripped away.

Figure 2a shows shadow masking for directionally deposited materials.

25 Figure 2b shows silver screen painting for sprayed or painted materials.

Figure 3 is a schematic view of a passive-matrix addressed organic electroluminescent display, as seen through the transparent substrate. The (transparent) anode is patterned in

columns and the cathode in rows. Pixels shine at the intersection of positively biased columns and one negatively biased row. The display is addressed row-by-row.

Figure 4a shows a first insulator and resin patterned in rows.

Figure 4b shows the insulator etched to form inter-insulators structure and resin stripped.

5 Figure 4c shows a stack of two insulators and the resin patterned in rows.

Figure 4d shows the top insulator etched by first method.

Figure 4e shows the bottom insulator etched by second method and resin stripped.

Figure 4f shows the OELs and cathode deposited. The cathode does not form a connection with anode even if flows above OELs edge.

10 Figure 4g is a detail of the rampart as described in Figure 4f.

Figure 5 shows the high-wall separator structure as taught in patent US 5,294,869.

Figure 6a shows a stack of two or more different insulators formed preferably by the same method, and patterned resin in accordance with the principles of the invention.

15 Figure 6b shows all the insulators being etched in same solution, the top one etching the one below to create the overhang.

Figure 6c shows how materials formed on top are discontinuous at the edges of the separators.

Figure 7a shows an anode formed and patterned in columns.

20 Figure 7b shows a stack of three insulators formed, preferably by the same method, and photosensitive resin patterning in rows.

Figure 7c shows pattern transfer to the stack of insulators by buffered hydrofluoric acid etching, which leaves an overhang and a tail-out.

Figure 7d shows the formation of organic electroluminescent layers and of the cathode by a directional deposition method which separates the cathode in rows.

25 Figure 8 is a scanning electron microscope picture of a section of the separator, the organic layers and the cathode. Note that the cathode extends over the edge of the organic layers so without the tail-out there would be a short circuit.

Figure 9a shows a stack of two insulators formed, preferably by the same method, and photosensitive resin patterning.

Figure 9b shows the pattern transfer to the stack of insulators by buffered hydrofluoric acid etching, which leaves an overhang.

- 5 Figure 9c shows how spin-on of polymer layer conserves overhang and discontinues polymer at separator edge.

Figure 10 is a scanning electron microscope picture of a section of the separator and the spun-on polymer.

Detailed Description of the Preferred Embodiments

- 10 Referring to Figure 6a, on a substrate on which inorganic structures may or may not have been previously formed, a stack of different inorganic layers 60, 62, 64 are deposited using preferably only one technique, though each layer or some of them could be deposited by different techniques (Fig 6a). The materials of the stack are chosen so as to all be etched in the same solution with different etching rates, or be etched by the same
15 dry etch method at different rates. The structures previously formed on the substrate should not be affected by this etch. A photosensitive resin layer formed on top of the insulators stack is then patterned by lithography; then the substrate is dipped into a solution that is capable of etching all the materials of the stack in a single etch step.

- The stack has at least two layers, with the top material 64 being etched slower than at
20 least one lower material, such that an overhang 66 is obtained (Fig 6b). Thanks to the overhang 66, a material incompatible with conventional microfabrication techniques can be deposited on top of this separator and be discontinuous at the edges of this separator (Fig 6c). Alternatively, a material compatible with standard microfabrication techniques could be deposited on top of one or several layers of materials incompatible with standard
25 microfabrication techniques and be discontinuous at the edge of the separator.

The physical vertical separation provided by the separator with the overhang for the materials deposited on top can be used for example as electrical insulation or optical discontinuity.

FIRST EXAMPLE

The first example of application of the separator is its use in an organic light emitting display addressed in a passive XY matrix as of the type shown in Figure 3. The method is described in Figures 7a to 7d. First a (transparent) anode 30 is formed and patterned in columns by conventional lithography (Fig 7a). The second step is the deposition of a stack 70 of three insulators in a single run using a commercial Plasma Enhanced Chemical Vapor Deposition (PECVD) system. The stack 70 consists of 2000Å of dense SiO₂, followed by 16,000Å of porous SiO₂, and top layer of 2000Å dense Si₃N₄. A photosensitive resin 72 is then spun on the sample and patterned in rows (Fig 7b); then the pattern is transferred by etching the stack of insulators in buffered hydrofluoric acid (Fig 7c). The top insulator etches slowly and when it has been etched away from the unmasked areas, the acid starts etching the middle insulator much faster and undercuts it, creating an overhanging profile 74. The lower insulator layer is etched at a slower rate than the middle one, which provides a tail-out 76. The photosensitive resin is stripped, then the organic layers and the cathode are thermally evaporated: 600Å of TPD (N, N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine) followed by 600Å of AlQ₃ (tris (8-hydroxy-quinolate) aluminum) and 1000Å of Al (Fig 7d).

Due to the directivity of the evaporation, the organic materials and the cathode are discontinuous at the edges of the separator previously patterned in rows, as seen in Figure 8. A test structure showed that the physical separation of the cathode could sustain 50V in air, which is much more than needed. In Figure 8 one can also appreciate that the cathode extends over the edge of the organic layers, which means that the matrix would be shorted without the tail-out.

SECOND EXAMPLE

Some organic materials of interest for electronic or optoelectronic applications are polymers that are hard to evaporate, but can be simply spun, for example using the spin-coaters that are used to form photosensitive resin films. The separator can be successfully used in this case also, and a method is described in Figures 9a to 9c. 16,000Å of porous SiO₂ followed by 2,000Å of dense Si₃N₄ are deposited in a single run using a commercial Plasma Enhanced Chemical Vapor Deposition (PECVD) system to form stack 70. In the same manner as in the first example, a photosensitive resin 72 is then spun on the sample and patterned (Fig 9a); then the pattern is transferred by etching the stack of insulators in

buffered hydrofluoric acid. The top insulator etches slowly and when it has been etched away from the unmasked areas, the acid starts etching the middle insulator much faster and undercuts it, creating an overhanging profile (Fig 9b). A polymer 74 is spun on it, sufficiently diluted in a solvent and spun at a speed such that its thickness on flat surfaces is about 1000Å. As shown in Figure 10, the overhanging profile is conserved and the polymer is discontinuous.

For polymers with electroluminescent properties, an anode can be formed prior to the separator. Electroluminescent polymer layer(s) are then spun on and a cathode can be deposited on top in the same manner as in the first example. The cathode is discontinuous at the edge of the separator, so if the anode has been formed in columns and the separators in rows, a XY passive matrix addressed polymer electroluminescent display is obtained.

The discontinuity of the spun organic material at the edge of the separator means that any shape the separator has been given will be replicated in the polymer. Thus, a conductive polymer could be patterned in this way to make any high resolution component.

I claim:

1. A method of forming one or more patterned layers of organic material on a substrate, comprising the steps of:
 - forming a composite stack of at least two inorganic layers on said substrate, said
 - 5 inorganic layers having different etch rates, with an upper layer having a lower etch rate than an underlying layer;
 - masking said composite stack to leave exposed portions thereof defining a pattern;
 - etching away said exposed portions of said composite layer to form separators with an overhang resulting from the different etch rates of said layers; and
 - 10 depositing an organic layer on the resulting structure to form a patterned organic layer between said separators.
2. A method as claimed in claim 1, wherein said stack comprises three said layers, with a lower said layer having a lower etch rate than a middle said layer to provide a tail out.
- 15 3. A method as claimed in claim 2, wherein said exposed portions are etched away in a single etch step.
4. A method as claimed in claim 3, wherein said etch step is a wet etch.
5. A method as claimed in claim 4, wherein said etch step is carried out with buffered hydrofluoric acid.
- 20 6. A method as claimed in claim 3, wherein said etch step is a dry etch.
7. A method as claimed in claim 1, wherein said organic layer is deposited using a directional deposition technique.
8. A method as claimed in claim 7, wherein said organic layer is deposited by evaporation through a shadow mask.
- 25 9. A method as claimed in claim 1, wherein said organic layer is polymer spun onto said resulting structure using a spin coater.
10. A method as claimed in claim 9, wherein said organic layer is a monomer or oligomer evaporated onto said resulting structure.

11. A method as claimed in claim 1, wherein said composite stack comprises three layers of different density or chemical composition to provide said different etch rates.
12. A method as claimed as claimed in claim 11, wherein said composite stack comprises a bottom layer of a dense silicon dioxide, a central layer of porous silicon
5 dioxide, and a top layer of silicon nitride.
13. A method as claimed in claim 12, wherein said inorganic layers are deposited by Plasma Enhanced Chemical Vapor Deposition.
- 14 A method as claimed in claim 1, wherein said composite stack is formed on a substrate provided with parallel strips forming electrodes, and said separators are formed
10 as vertical walls with overhanging parts extending across said strips to form an array.
15. A method as claimed in claim 14, wherein said organic material is an electroluminescent material.
16. A method as claimed in claim 1, wherein a metal layer is deposited on said one or more organic layers such that said overhang vertically separate portions of the metal
15 layer.
17. A method as claimed in claim 16, wherein said metal layer is an aluminum layer.
18. A method of fabricating an electronic device, comprising the steps of:
forming a composite stack of at least two inorganic layers on a substrate, said
inorganic layers having different etch rates, with an upper layer having a lower etch rate
20 than an underlying layer;
masking said composite stack to leave exposed portions thereof defining a pattern;
etching away said exposed portions of said composite layer to form separators
with an overhang resulting from the different etch rates of said layers;
depositing at least one patterned layer including one or more organic layers on the
25 resulting structure; and
depositing an electrode layer on said organic layer, wherein portions of said
electrode layer deposited on said organic layer between said separators are vertically
separated from remaining portions of said electrode layer, which are deposited on said
separators.

19. A method as claimed in claim 18, wherein said organic layer is deposited using a directional technique.
20. A method as claimed in claim 18, wherein said organic layer is deposited by evaporation through a shadow mask.
- 5 21. A method as claimed in claim 18, wherein said organic layer is deposited by spin coating.
22. An electronic device comprising at least one patterned layer of organic material, and separators separating portions of said at least one patterned layer, said separators comprising a stack of layers of inorganic material having different etch rates, an upper
10 layer of said stack having a lower etch rate than a lower layer.
23. An electronic device as claimed in claim 22, wherein said at least one patterned layer is formed on a plurality of strips forming electrodes, and said separators are in the form of walls with overhangs extending across said strips to form an array.
24. An electronic device as claimed in claim 23, wherein said organic material is an
15 electroluminescent material, and said device is an optoelectronic device.

Figure 1a

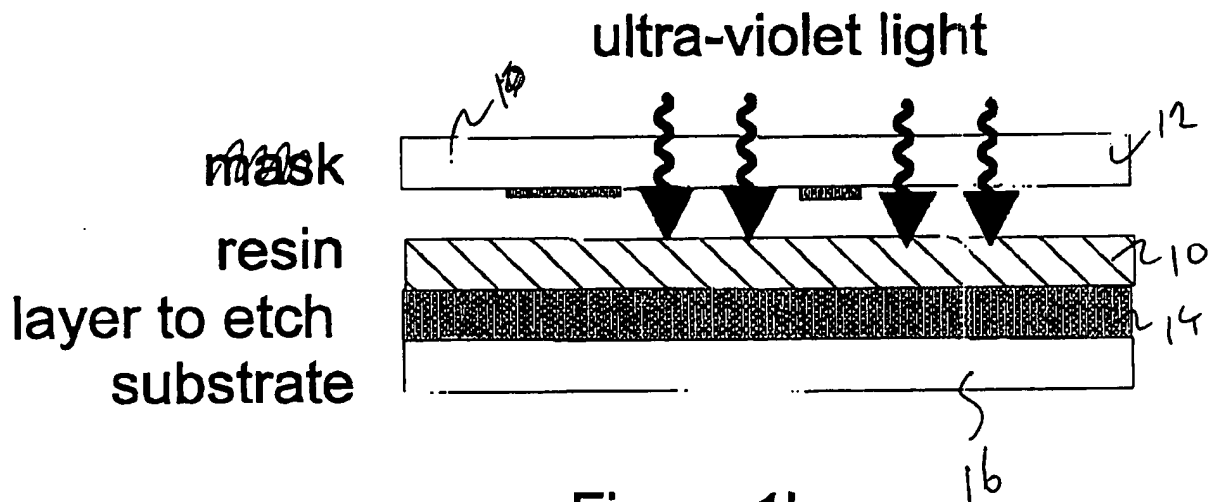


Figure 1b

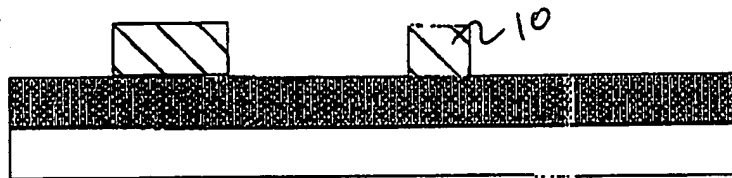


Figure 1c

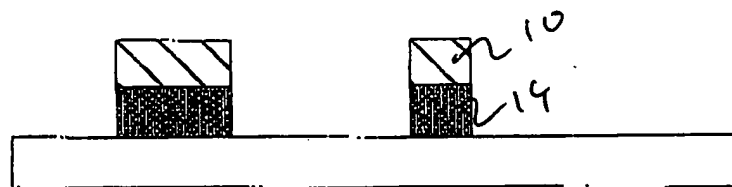


Figure 1d



PRIOR ART

Figure 2a

material deposited by a directional method

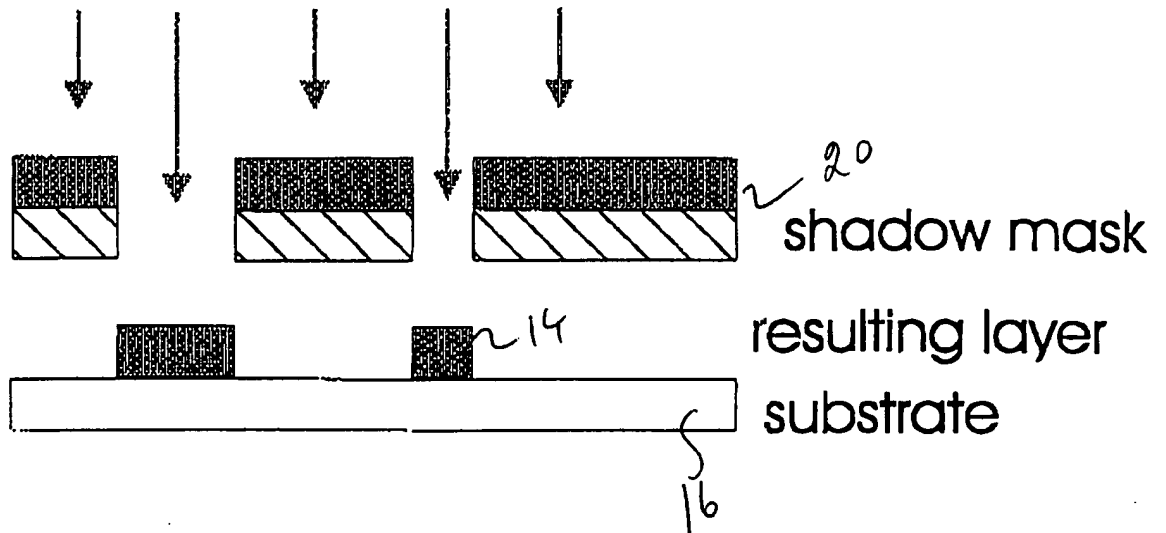
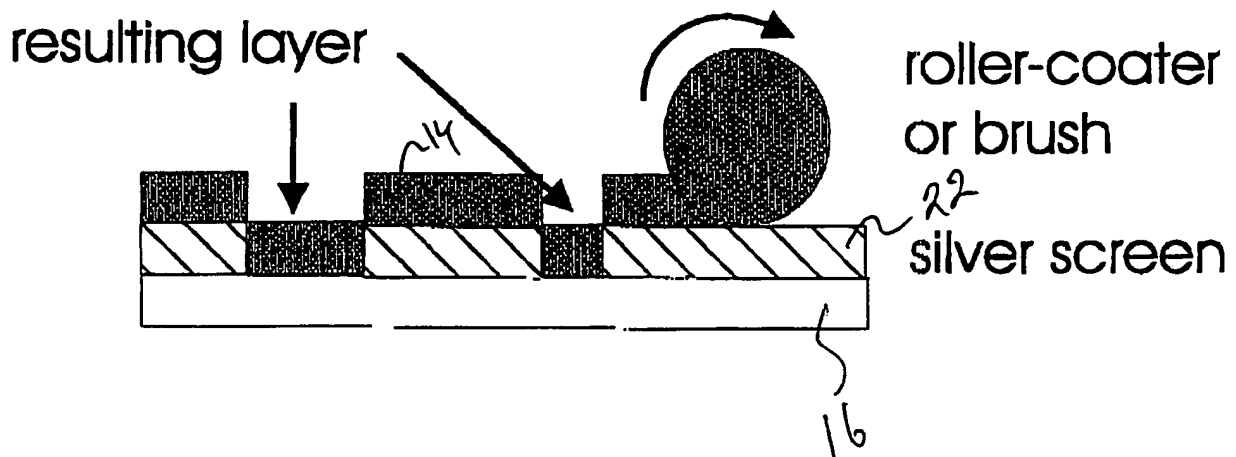
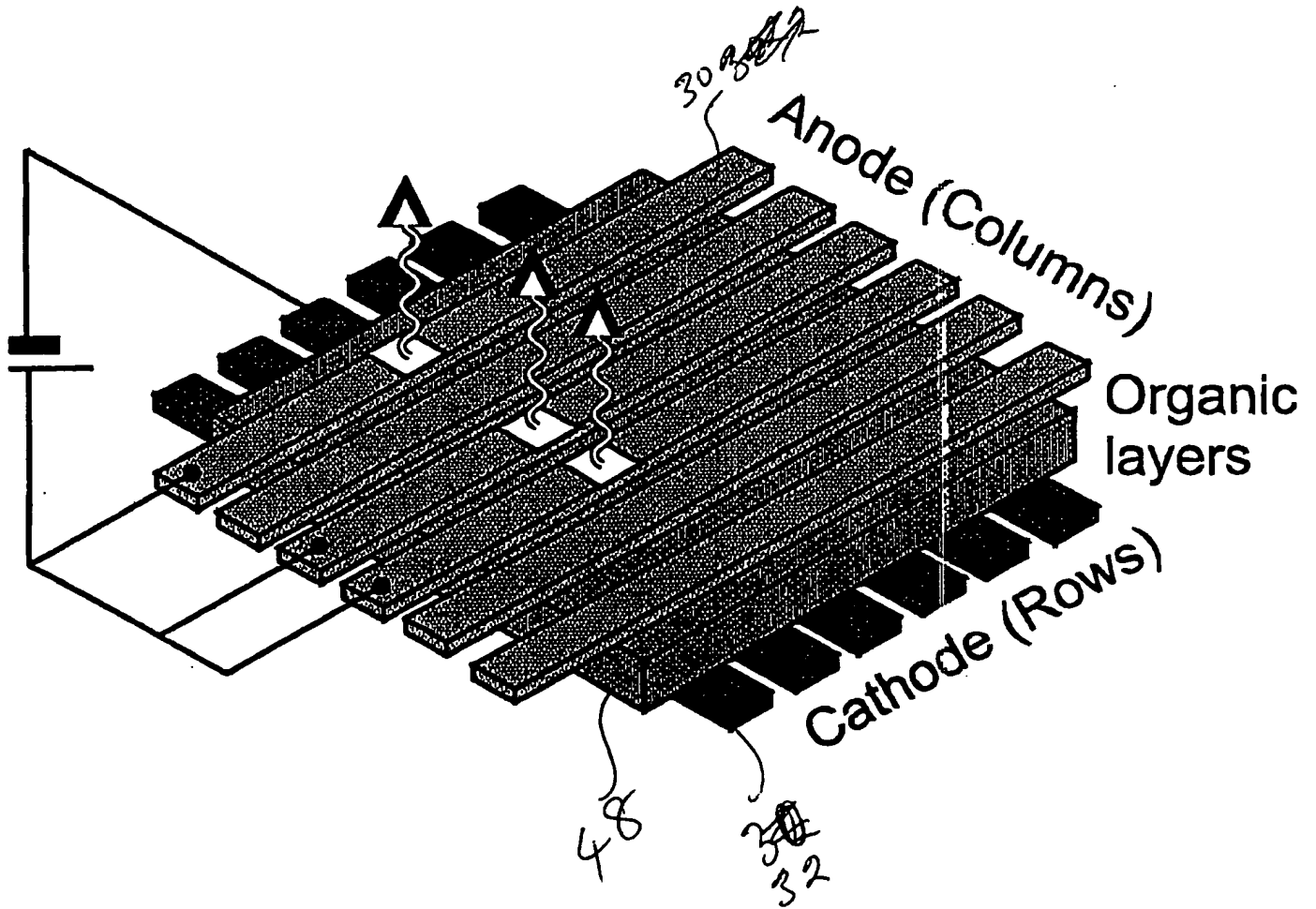


Figure 2b



PRIOR ART

Figure 3



PRIOR ART

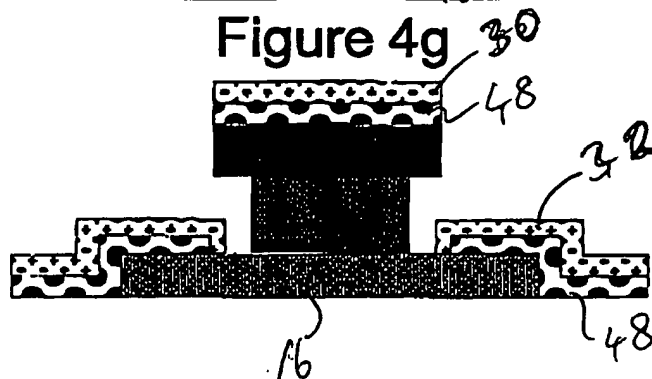
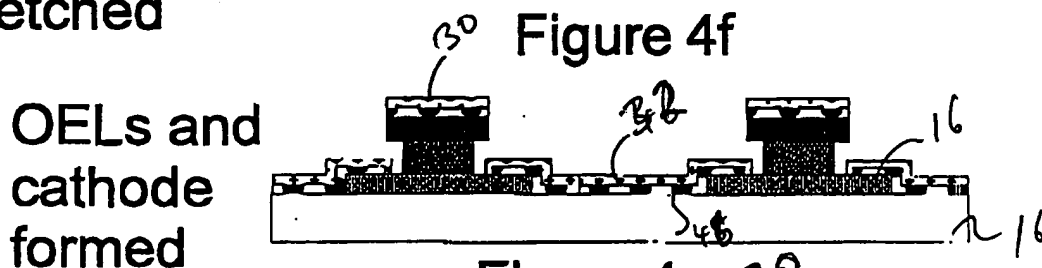
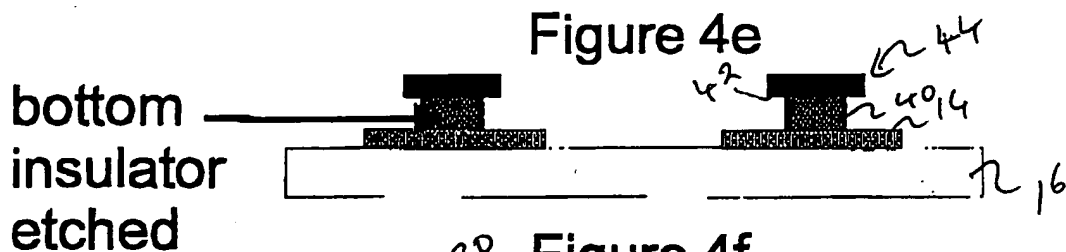
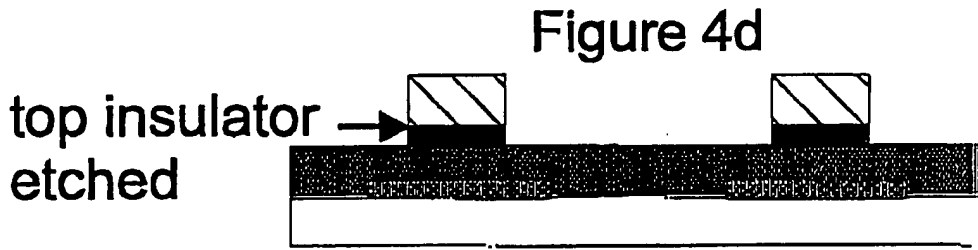
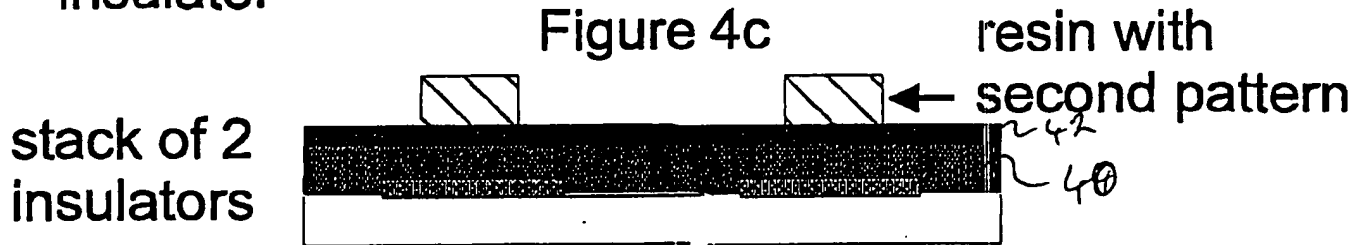
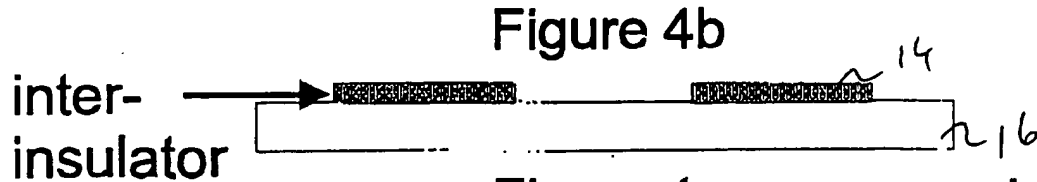
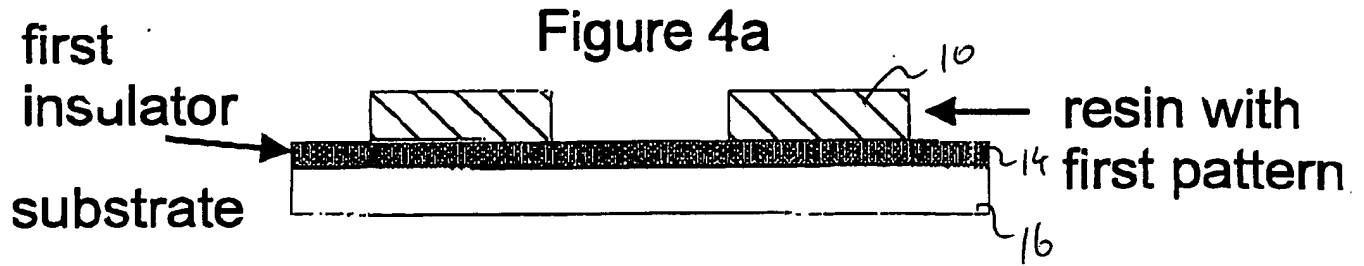


Figure 5

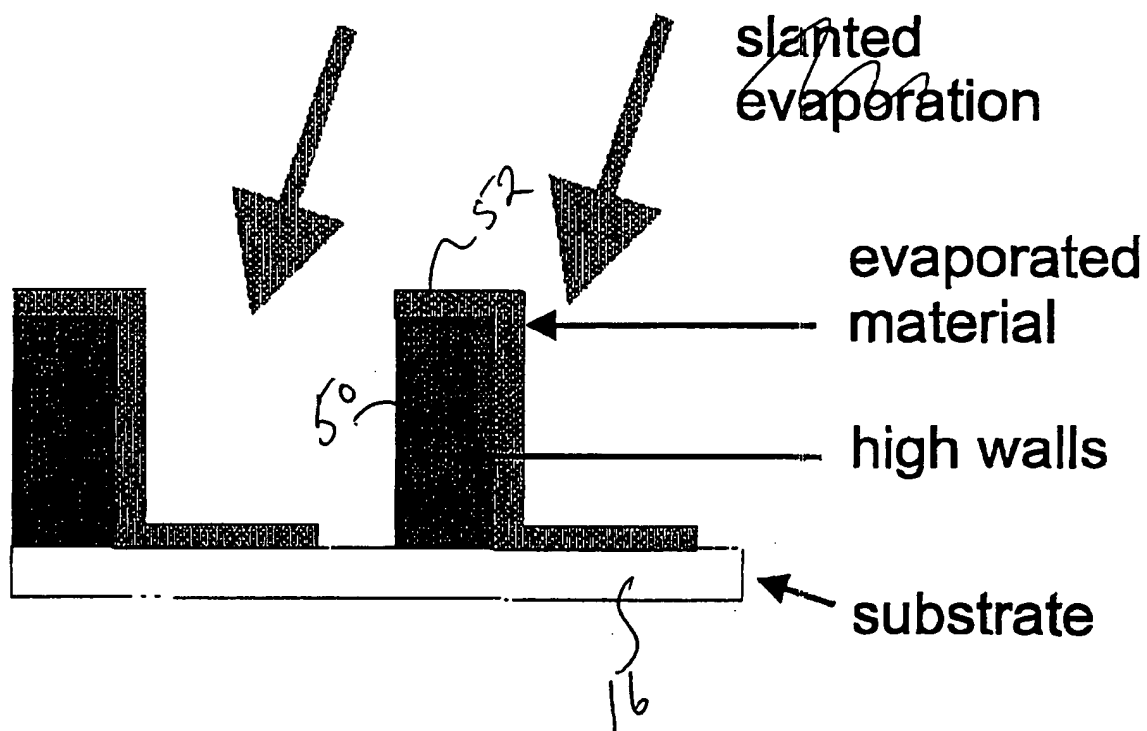


Figure 6a

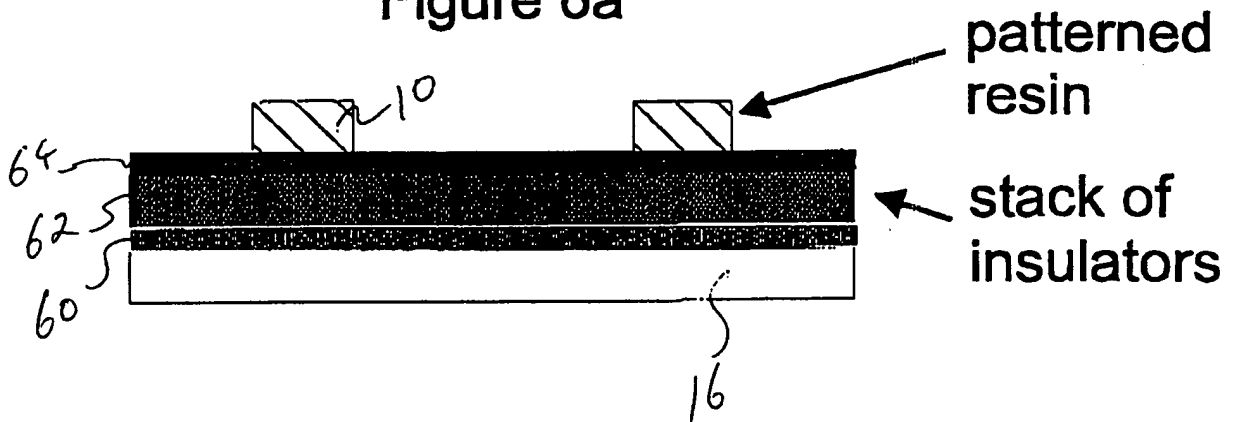


Figure 6b

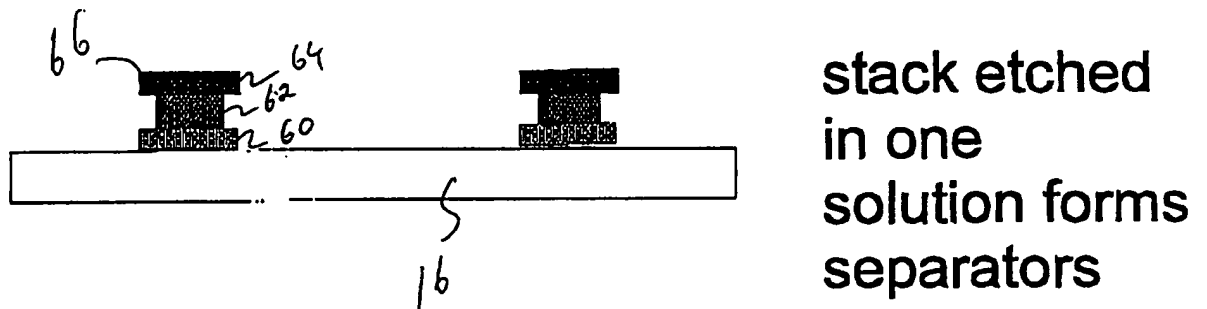


Figure 6c

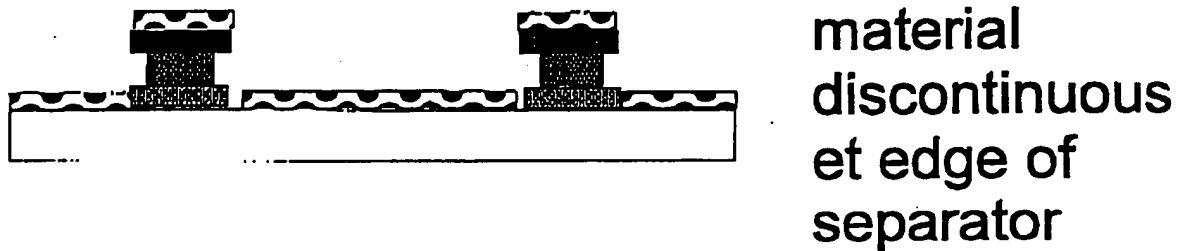


Figure 7a

anode patterned
in columns

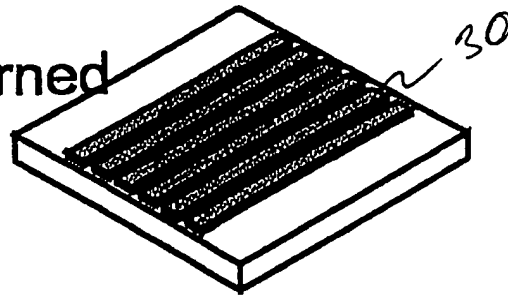


Figure 7b

resin patterned in rows

stack of
insulators

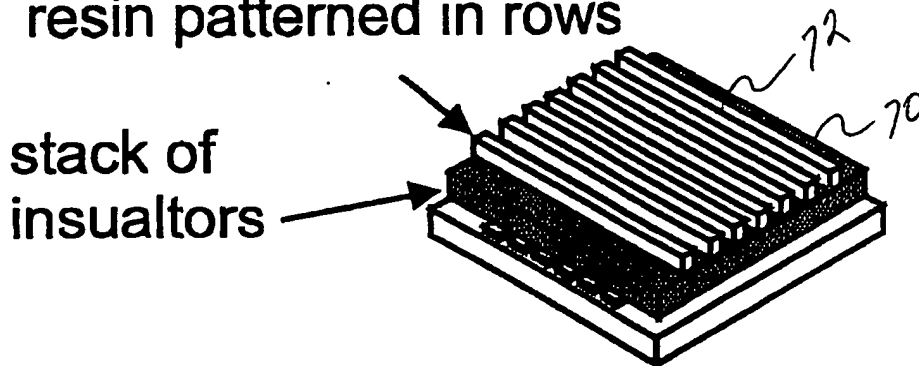


Figure 7c

stack etched in
one solution
form separators

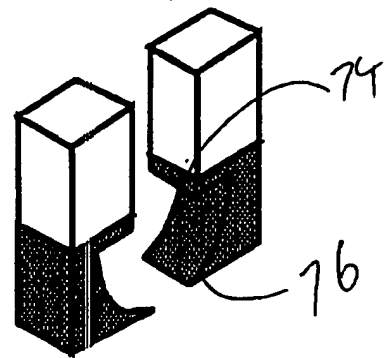
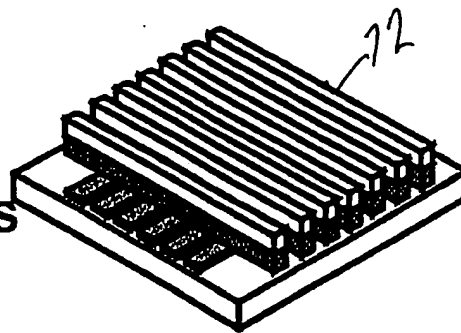


Figure 7d

OELs and cathode

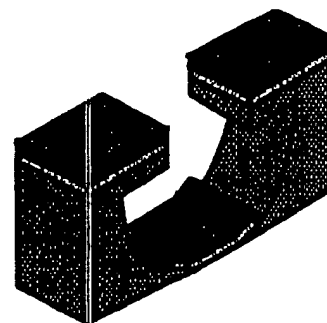
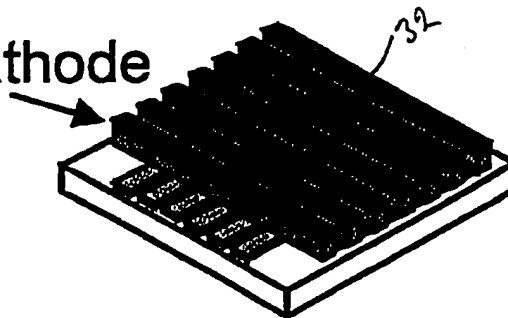


Figure 8

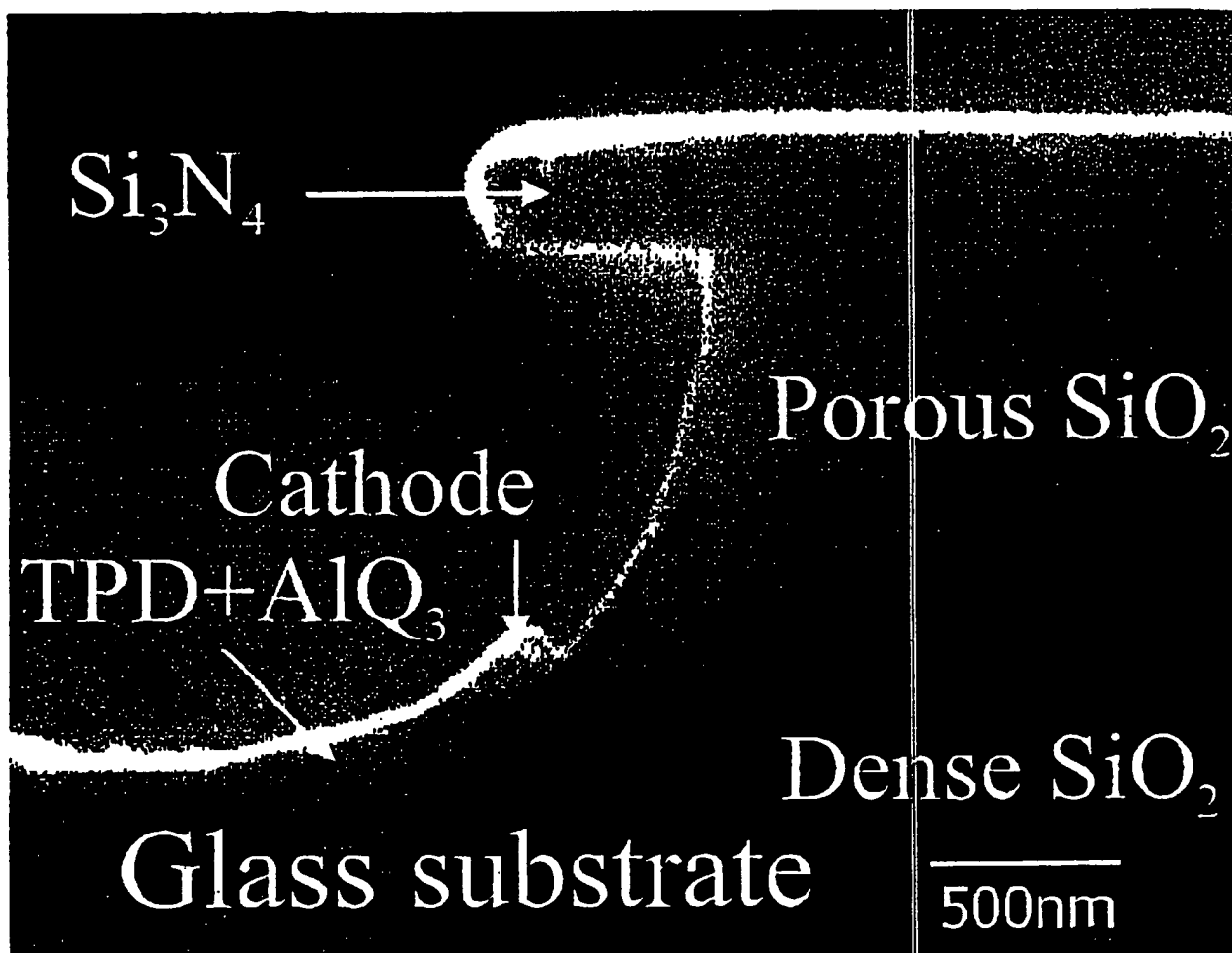


Figure 9a

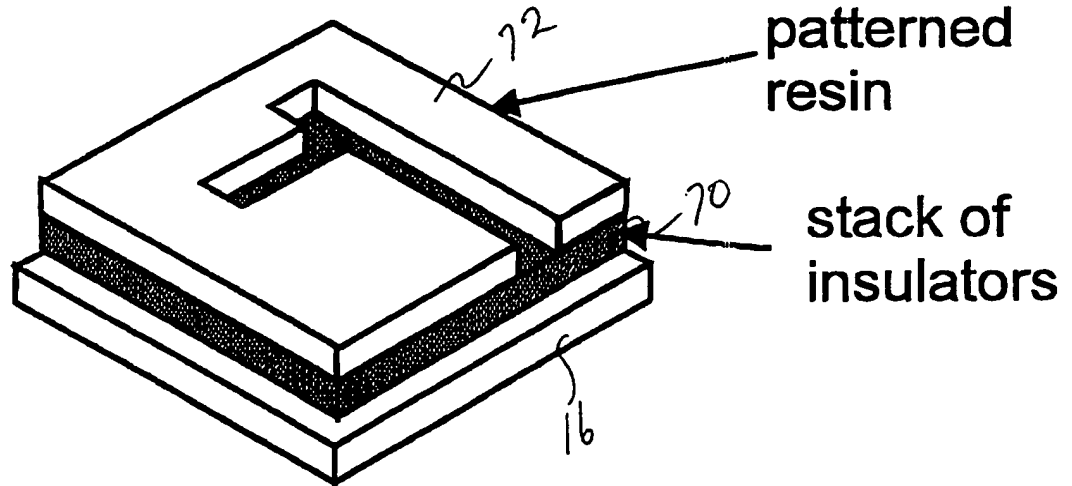


Figure 9b

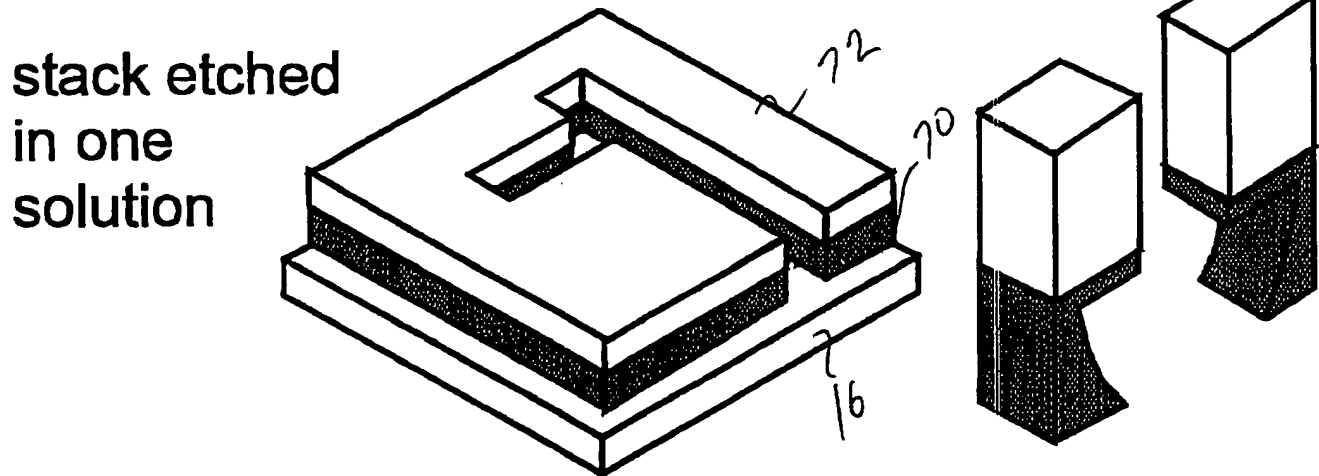
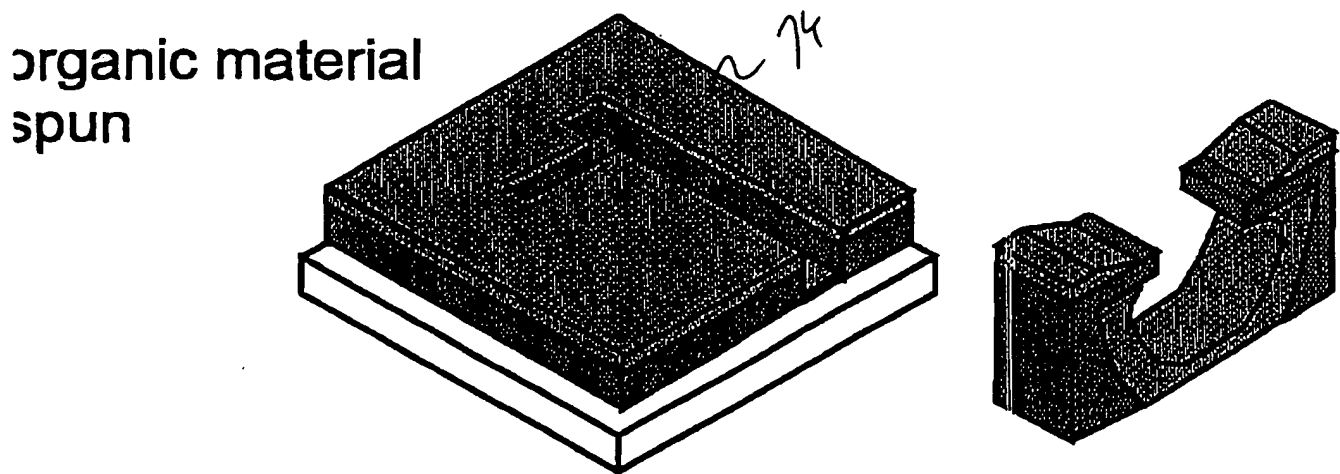


Figure 9c



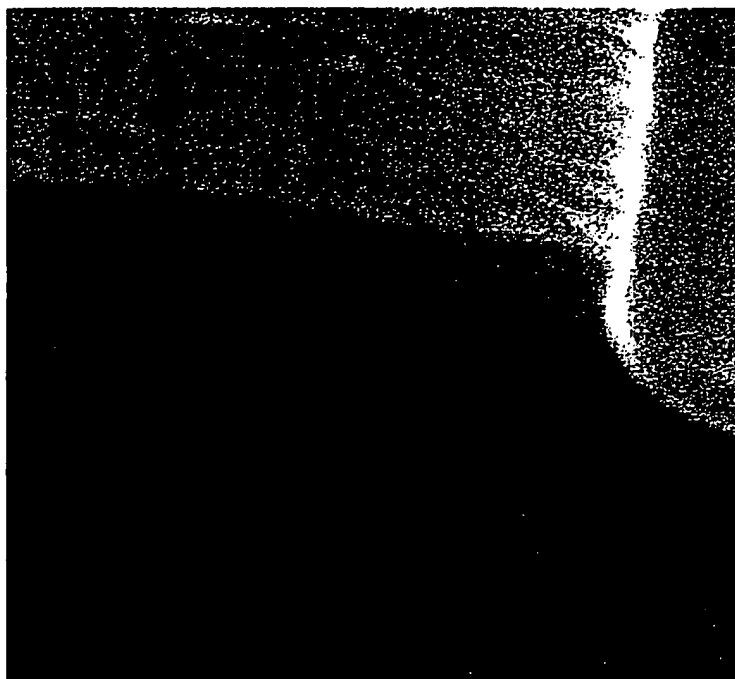


Fig. 10